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COMPLETE SPECIFICATION.

Improvements in or relating to Spent Pickling Acids.

We, THE STEEL COMPANY OF WALES LIMITED, of Abbey Works, Port Talbot, in the County of Glamorgan, Wales, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to the disposal of spent pickling acids after use in the treatment of iron or steel for various purposes requiring the production of a chemically clean metallic surface.

The disposal of spent pickling acids consisting mainly of iron salts and a certain amount of free acid has been a problem in steel works practice for many years because the cost of recovery of the iron salts and acid has been excessive in relation to the value of the materials and yet it is not permissible to allow it to run to waste owing to the danger of fouling rivers and streams.

The present invention provides an economic method of recovery in which the acid is obtained in a concentration in which it can be re-used in the pickle line and the iron is obtained in the form of a solid salt suitable for use in acid regeneration plants.

The concentration by evaporation of waste pickle liquor consisting of an aqueous solution of sulphuric acid and ferrous sulphate is rendered difficult by the progressive precipitation of large quantities of the mono-hydrate of ferrous sulphate.

A process has been proposed for regeneration of these spent pickle liquors by continuously adding spent acid liquor to a 40% to 60% solution of sulphuric acid heated by a submerged flame burner so as constantly to evaporate water therefrom and removing precipitated ferrous sulphate and accumulated regenerated sulphuric acid solution therefrom as they are formed, the rate of addition of said spent liquor and the rate of

evaporation from said sulphuric acid being regulated so as to maintain the sulphuric acid concentration.

The present invention is based upon the principle of first precipitating and separating the ferrous sulphate in a vessel without any reheating by means of the admixture of concentrated sulphuric acid (e.g. B.O.V.) and only after the separation of the ferrous sulphate evaporating the remaining aqueous solution of sulphuric acid in the same or a separate vessel.

According to the present invention therefore, a process for the recovery of sulphuric acid from waste pickle liquor comprises raising the acid concentration of the said liquor with concentrated sulphuric acid to precipitate ferrous sulphate, separating the latter and withdrawing with it mother liquor containing an amount of acid, substantially equal to that contained in waste pickle liquor treated, and thereafter evaporating the remaining mother liquor by the application of heat and utilising the steam generated for heating pickling tanks and the concentrated acid for further precipitation of ferrous sulphate; the acid withdrawn with the ferrous sulphate being separated from the latter and used in the pickle line. In order to ensure that the maximum amount of ferrous sulphate is precipitated, the concentration of the liquor is preferably increased to above 55% W/W of sulphuric acid.

In one method of carrying out the invention, waste pickle liquor containing approximately 12% W/W of sulphuric acid is added to hot concentrated sulphuric acid (B.O.V.) already present in the recovery vessel in an amount such that the resulting mixture has a concentration of not less than 55% W/W of sulphuric acid. The ferrous sulphate mono-hydrate precipitated is removed from the bottom of the vessel, together with a portion of the sulphuric acid mother liquor

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as above described. Thereafter, the remaining solution of sulphuric acid is evaporated by means of a steam coil or other suitable method until the strength again reaches B.O.V., when a further addition of waste pickle liquor can be made, as described above.

In the arrangement set out above, the sulphuric acid used for precipitation remains in the one vessel which is preferably of considerable height in relation to the diameter, so that waste pickle liquor may be added towards the top of the vessel and ferrous sulphate withdrawn from bottom. In this arrangement, however, the addition of waste liquor and withdrawal of ferrous sulphate has to be interrupted in order to concentrate the mother liquor remaining in the vessel. In an alternative arrangement the mother liquor may be concentrated in a separate vessel and the concentrated acid liquor returned to the precipitating vessel simultaneously with the addition of a further quantity of waste pickle liquor.

The ferrous sulphate obtained in the process above described is separated from the sulphuric acid with which it is associated by suitable means, for example, centrifuge and the acid recovered thereby is returned to the pickle line. The ferrous sulphate is particularly suitable for use in acid regeneration plants where the iron sulphate is converted into iron oxide and sulphuric acid.

The evaporated steam is used for heating the pickling tanks.

What we claim is :—

1. A process for the recovery of sulphuric acid from waste pickle liquor which comprises

raising the acid concentration of the liquor with concentrated sulphuric acid to precipitate ferrous sulphate, separating the latter and withdrawing with it mother liquor containing an amount of acid substantially equal to that contained in the waste pickle liquor treated, and thereafter evaporating the remaining mother liquor by the application of heat and utilising the steam generated for heating pickling tanks and the concentrated acid for further precipitation of ferrous sulphate; the acid withdrawn with the ferrous sulphate being separated from the latter and used in the pickle line.

2. A process as claimed in Claim 1, wherein the concentration of the liquor is raised to above 55% W/W of sulphuric acid, whereby substantially all the ferrous sulphate is precipitated.

3. A process as claimed in Claim 2, wherein the waste liquid with a concentration of approximately 12% W/W sulphuric acid is added to hot concentrated sulphuric acid (for example, B.O.V.) in an amount such that the resulting mixture has a concentration of not lower than 55% W/W of sulphuric acid, and after the removal of the ferrous sulphate precipitated the remaining acid is evaporated until the strength again reaches B.O.V. concentration.

4. A process for the recovery of sulphuric acid from waste pickle liquor, substantially as hereinbefore described.

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PROVISIONAL SPECIFICATION.

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We, THE STEEL COMPANY OF WALES LIMITED, of Abbey Works, Port Talbot, in the County of Glamorgan, Wales, a British Company, do hereby declare this invention to be described in the following statement :—

This invention relates to the disposal of spent pickling acids after use in the treatment of iron or steel for various purposes requiring the production of a chemically clean metallic surface.

The disposal of spent pickling acids consisting mainly of iron salts and a certain amount of free acid has been a problem in steel works practice for many years because the cost of recovery of the iron salts and acid has been excessive in relation to the value of the materials and yet it is not permissible to allow it to run to waste owing to the danger of fouling rivers and streams.

The present invention provides an economic method of recovery in which the acid is obtained in a concentration in which it can be used further in recovering spent acid and the iron is obtained in the form of a solid salt suitable for use in acid regeneration plants.

The concentration by evaporation of waste pickle liquor consisting of an aqueous solution of sulphuric acid and ferrous sulphate is rendered difficult by the progressive precipitation of large quantities of the monohydrate of ferrous sulphate.

The present invention is based upon the principle of first precipitating and separating the ferrous sulphate in a vessel by means of the admixture of concentrated sulphuric acid (B.O.V.), and thereafter evaporating the remaining aqueous solution of sulphuric acid in the same vessel.

According to the present invention, a process for the recovery of sulphuric acid from waste pickle liquor comprises raising the acid concentration of the liquor with concentrated sulphuric acid in sufficient quantity to precipitate substantially all the ferrous sulphate, separating the latter, along with an amount of acid equivalent to that contained in the waste pickle liquor, evaporating the mother liquor and utilising the steam generated for heating pickling tanks and the concentrated acid for further precipitation of ferrous sulphate.

In order to ensure that the maximum amount of ferrous sulphate is precipitated, the concentration of the liquor is preferably increased to above 55% W/W of sulphuric acid.

In carrying out the invention, waste pickle liquor containing approximately 12% W/W of sulphuric acid is added to hot concentrated sulphuric acid (B.O.V.) already present in the recovery vessel until the resulting mixture has a concentration of at least 55 W/W of sulphuric acid. The ferrous sulphate monohydrate precipitated is removed from the bottom of the vessel, together with a portion of the sulphuric acid equivalent to that contained in the waste pickle liquor. Thereafter, the remaining solution of sulphuric acid

is evaporated by means of a steam coil until the strength again reaches B.O.V., when a further addition of waste pickle liquor can be made, as described above.

In the arrangement set out above, the sulphuric acid used for precipitation remains in the one vessel which is preferably of considerable height in relation to the diameter, so that waste pickle liquor may be intermittently or continuously added towards the top of the vessel and ferrous sulphate withdrawn from the bottom. In an alternative arrangement the mother liquor from the ferrous sulphate may be concentrated in a separate vessel and returned to the precipitating vessel.

The ferrous sulphate obtained in the process above described is particularly suitable for use in acid regeneration plants where the iron sulphate is split up into iron oxide and sulphuric acid.

The evaporated steam is used for heating the pickling tanks.

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